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# FUELS AND CHEMICALS FROM BIOMASS USING SOLAR THERMAL ENERGY

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## ABSTRACT

In the manufacture of fuels and chemicals from biomass, a significant fraction of the energy input to the processes is derived either from fossil fuels or from a portion of the biomass feedstock itself. Since there is a strong motivation for the U.S. to reduce where possible the use of fossil fuels for process energy, and since the use of biomass simply as a fuel is a suboptimal use of this feedstock, the employment of solar heat for process energy represents genuine conservation of these valuable resources. The most significant nearer term opportunities for the application of solar thermal energy to the manufacture of fuels and chemicals from biomass are summarized in this paper, with some comments on resource availability, market potential and economics. Special consideration is given to the production of furfural from agricultural residues, and the future role of furfural and its derivatives as a replacement for petrochemicals in the plastics industry.

## INTRODUCTION

Agricultural wastes offer a large source of available biomass. The Quaker Oats Co. has been active since the 1920's in the utilization of such waste products as a source of the chemical furfural. Current furfural processes convert only a portion of the collected raw material to the desired product with resultant by-production of large amounts of residues which on burning give sufficient energy to drive the process. The use of solar thermal energy for biomass processing would allow complete utilization of these residues for further conversion to higher value liquid fuels and chemicals.

Solar energy is considered to be the most viable source of process energy for totally integrated biomass plants in the future. Since most, if not all, of the biomass is to be converted to furfural and other chemical derivatives, or to high utility value convenience fuels for transportation, an alternate source of energy is needed. Since it is anticipated that these plants will be relatively small, to minimize collection costs of the biomass, coal does not appear to be a viable heat source because of transportation and pollution control problems. Solar energy therefore is considered to be the most viable long-term energy source.

The study presented in this paper is part of a proposed project aimed at determining the feasibility and optimum design of an integrated process for the production of fuels and chemicals utilizing agricultural residues. An important feature of fuels and chemicals based on furfural and its co-products is that the feedstocks are agricultural wastes and, as a result, do not compete with the food supply. The proposed study, to be conducted by IIT Research Institute with the cooperation of the Quaker Oats Co. and the consultation of Prof. M. Wayman of the University of Toronto, will indicate the best approaches for maximizing the energy yield of the biomass with the use of concentrated solar heat as the primary source of process energy. The potential of furfural and its derivatives as "renewable resource" chemicals to replace petrochemicals in the production of plastics and elastomers is also considered.

## SOLAR POWERED BIOMASS CONVERSION PROCESS

Biomass, regardless of source, consists primarily of three principal ingredients, namely, hemicellulose, cellulose and lignin. Agricultural residues such as corncobs, sugar bagasse and oat hulls, as well as hardwoods, give hemicelluloses which contain relatively large amounts of pentosans (C-5 sugars) which can be cleaved and dehydrated to give furfural, a pseudo-aromatic chemical which has the potential of replacing petroleum derived benzenoid chemicals and resins. Softwood hemicelluloses, by contrast, consist essentially of hexosans (C-6 sugars) which do not yield furfural, but which can be fermented to alcohol, usuable as a liquid fuel. These hemicelluloses are rather easily hydrolyzed to a mixture of fermentable sugars such as glucose and mannose. Cellulose, by contrast, consists of essentially 6 carbon glucose units linked together by $\beta$ linkages which permit the molecules to orient to give highly crystalline structures which are quite resistant to hydrolysis to simple sugars.

Lignin consists primarily of propenylphenol moieties linked by a number of different bonds, including ether linkages and carbon-carbon bonds. The lignin is closely associated with the cellulose portion, possibly with direct chemical bonds, so much so that some researchers in the field regard lignin as a "glue" that holds the cellulose structure together. Once isolated by mechanical/chemical means, lignin is soluble in alkaline solutions via salt formation with the phenolic hydroxyls.

Currently two industries process large quantities of biomass for non-food uses: The forest products industry pulps wood to separate the cellulose from the hemicellulose and lignin fractions, primarily for use in making paper, but also for chemical conversion to rayon fibers, cellophane film, and acetate plastics. The Quaker Oats Company processes agricultural residues so as to convert the pentosan hemicellulose fraction into furfural. These industries use different fractions of the collected biomass and convert only a portion of the huge amount of biomass they process into useful products. From 50 to 90% of the total biomass collected is burned as fuel. The challenge of a solar powered biomass conversion process is to maximize the energy yield of the biomass by complete utilization with the use of concentrated solar heat as the primary source of process energy for the production of chemicals and liquid fuels.

An integrated biomass conversion process would separate the components in an undegraded state so that subsequent processing would result in liquid fuels and chemical products of greater value. Unavailability of by-products as fuel, however, would require substitution of energy from another source. Solar-thermal energy can provide the steam needed for biomass processing and energy for product distillation and purification.

The critical aspect of such a biomass conversion process is the separation of biomass into hemicellulose, cellulose and lignin under conditions which do not degrade these fractions during separation. An effective pretreatment is "autohydrolysis" (ref. 1), which consists of steaming the biomass at about 200°C for approximately 20 minutes. This breaks up the crystallinity of the cellulose, renders the hemicellulose soluble in hot water, and partially depolymerizes the lignin which becomes soluble in dilute sodium hydroxide solution from which it can be separated by acidification. The cellulose freed from hemicellulose and lignin is separated in a partially decrystallized form suitable for hydrolysis. The hemicellulose filtrate would be diverted to an existing Quaker Oats plant, the lignin would be sent to a conversion unit for the production of useful chemical intermediates, and the cellulose would go to a saccharification/fermentation plant for conversion to alcohol fuel. A tentative process flowsheet is shown in fig. 1.

For continuous operation during cloudy or non-daylight hours, in the absence of a thermal storage system, some of the residual lignin which has a high heat of combustion (~11,000BTU/lb), could be effectively utilized as supplemental fuel for hybrid operation.

## BIOMASS RESOURCE AVAILABILITY

Agricultural crop residues in the US amount to about 1 billion tons annually. While a portion of this is re-used in agriculture itself, the potential is there to produce 5-10% of the nation's energy needs from these wastes. Thus, biomass now existing can provide substantial amounts of feedstocks to processes such as the one described here.

Corncobs are the preferred material because of optimum furfural production and relative ease of grinding and processing. However, widespread use of combines to harvest corn has drastically reduced the availability of cobs. A possible future raw material would be the "corn stover" which exits from the combine when corn is harvested. Alternate feedstocks might be sugar bagasse or aspen chips. For the longer term, processing of guayule bagasse after extraction to remove rubber-like hydrocarbons will be considered. Guayule has been proposed as a viable source of "rubber latex" which can be grown on currently nonproductive arid regions in the southwestern U.S. Since these are areas of high insolation, application of solar thermal energy to the processing of guayule may be particularly advantageous. The fibers extracted from guayule bagasse contain relatively high levels of pentosans which could be converted to furfural. Subsequent removal of lignin would yield fibers suitable for paper (based on USDA studies) or for saccharification and fermentation to alcohol.

## ALTERNATIVE FUELS AND CHEMICALS

In addition to developing alternative fuel sources, alternative chemical process feedstocks must be developed if dependence on petroleum imports from OPEC nations is to be eliminated. Furfural is a very versatile chemical which can be utilized in a variety of synthetic organic processes. Furfural is used as is as a selective solvent for refining motor lube oil, but is used more extensively as a feedstock for producing other chemicals such as furfuryl alcohol, tetrahydrofurfuryl alcohol, furan, tetrahydrofuran, and polybutylene glycol ethers. Until fairly recently, THF via furfural was the feedstock for du Pont's Nylon 6/6. Currently the largest market for chemicals based on furfural is for furfuryl alcohol which on condensation gives a resinous binder.

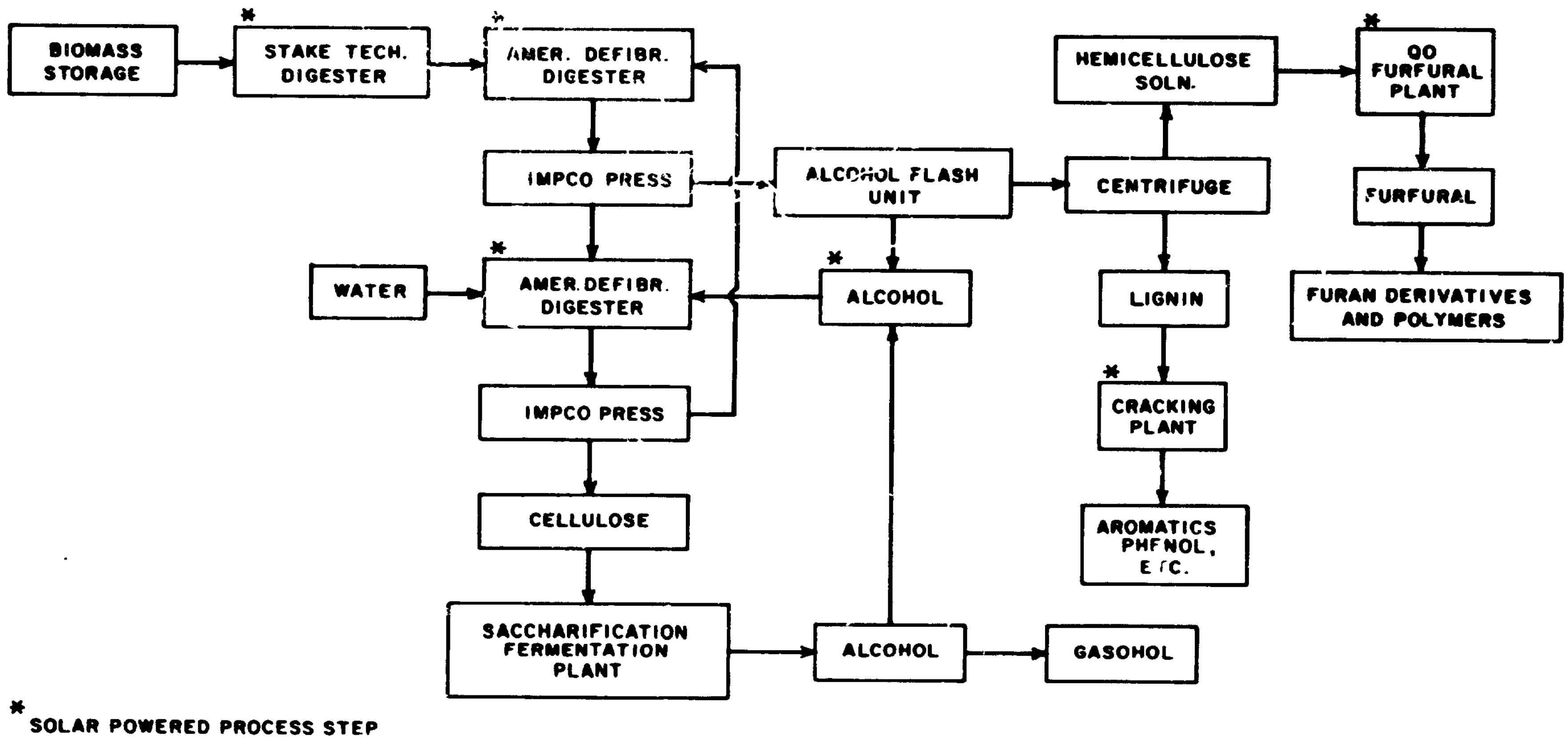


FIGURE 1. SOLAR-POWERED BIOMASS CONVERSION FLOWSHEET

The furan ring is pseudo-aromatic and undergoes many of the reactions of analogous aromatic compounds. Furfural and derivatives therefrom offer great potential for replacement of benzenoid chemicals such as styrene and phenol widely used in polystyrene and ABS plastics, in SBR elastomers, in phenolic molding compounds and plywood adhesives, and in polyester laminates. The pseudo-aromatic furan ring contributes many of the physical and chemical properties resulting from the aromatic benzene ring in petroleum based derivatives. Furfuryl alcohol resins could be used to replace phenolic resins as binders for particleboard and glue for plywood. With the price of phenol rapidly increasing and continued supply of phenol uncertain, the forest product industry currently is seeking a "renewable resource" adhesive to replace phenolics. Preliminary laboratory studies indicate that a furan resin can indeed be readily substituted for currently used phenolic adhesives. In order to supply this market, however, current production capacity of furfural/furfuryl alcohol, which is currently ~200 million lbs/yr, would need to be expanded by a factor of at least 10. Another potential large volume market for furfural is the production of vinylfuran as a replacement for styrene. Styrene, which is vinylbenzene, is a vital chemical intermediate for polystyrene plastics, insulating foams, elastomers and polyester resins for fiberglass laminates.

Thus, furfural appears to be a viable "renewable resource" alternate for the plastic industry. Potential large volume markets exist for the replacement of oil-derived aromatic chemicals. This increased volume of furfural could only be produced economically by development and construction of plants designed for the total utilization of biomass. It would appear that the economics and future outlook for such plants depend upon the availability of a source of energy not involving either fossil fuel or the combustion of the biomass itself. Solar heat has a contribution to make by providing the source of energy required for biomass conversion.

## REFERENCE


1. Wayman, M., 4th International Alcohol Fuels Symposium, Sao Paulo, Brazil, October 5-8, 1980.